

The Effect of Mercuric Iodide and Ammonium
Chloride on Glass

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY

CLARA EMILIE MILLER

BALTIMORE, 1930

[Reprinted from The Journal of Physical Chemistry, 35, 2985 (1931)]

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THE EFFECT OF MERCURIC IODIDE AND AMMONIUM CHLORIDE ON GLASS*

Introduction

In 1928 J. Rinse¹ measured the vapor pressure of mercuric iodide over a long temperature range (130°-347°C.) by a static method, using a glass-spring indicator. He obtained a continuous vapor pressure-temperature curve instead of one showing a sharp break between the saturation curve and the Boyle-Gay-Lussac curve for gases; in other words, at temperatures in the vicinity of the saturation point, the vapor pressure of the iodide was considerably lower than was expected. This was the same phenomenon noticed by McHaffie and Lenher² in the case of water vapor and of toluene vapor, and they explained it by the adsorption of the vapors on glass which took place to an increased extent in the neighborhood of the dew-point.

In all of these cases it would be necessary to assume that the adsorbed layer was several hundred molecules thick in order to account for the observed lowering of the vapor pressure but this assumption does not seem correct since it is improbable that the unsaturated forces at the surface of the glass extend to such a distance. However, several years ago Frazer, Patrick and Smith³ demonstrated the difference between a freshly fused glass surface and one chemically corroded. They showed that there was no more than a unimolecular layer of toluene adsorbed on a glass surface which was molecularly plane, whereas the adsorption was great and the vapor pressure followed a curve similar to those obtained by McHaffie and Lenher when the glass had been treated with chromic acid cleaning solution. The chromic acid-sulfuric acid mixture so etched and corroded the glass by removing alkali from it that capillary condensation took place. Water vapor itself also has this effect.

Altho Rinse⁴ found that etching by water vapor could not account for the shape of the curves he obtained, the possibility remains that in his experiments the mercuric iodide itself attacked the glass. With this point in mind, he made an effort to determine whether there was any chemical action between glass and mercuric iodide by placing a known weight of the latter in a glass tube, heating it to 600°C., recovering the iodide by subliming it into the tip of the tube, and reweighing it. He found that the same weight of the iodide could be recovered as was originally placed in the tube and concluded that no

¹ Smits and Rinse: *Rec. Trav. chim.*, **47**, 35 (1928).

² McHaffie and Lenher: *J. Chem. Soc.*, **127**, 1559 (1925); **1926**, 1785; **1927**, 272.

³ Frazer, Patrick and Smith: *J. Phys. Chem.*, **31**, 897 (1927).

⁴ Rinse: *J. Chem. Soc.*, **1928**, 1442.

chemical action had taken place. Nevertheless, sufficient reaction might have occurred to roughen the surface of the glass without causing any change in mass as far as could be determined by weighing to tenths of a milligram. The method used by Frazer, Patrick and Smith¹ and later by Latham² to demonstrate the action of cleaning solution on glass was therefore used again to show the effect of mercuric iodide and also of ammonium chloride on a glass surface.

Experimental

The experimental procedure was essentially the same as that first used by McHaffie and Lenher³ and it is described by them as well as by Frazer, Patrick and Smith⁴ and Latham.⁵ A definite volume of dry air-free toluene was enclosed in a pyrex bulb which had been fused and blown thru phosphorus pentoxide to prevent access of moisture and which therefore had a molecularly plane surface. The bulb was closed off from the rest of an evacuated system by means of a mercury U-tube which also served as a manometer to measure the vapor pressure of the toluene. Both the bulb and the U-tube were in a thermostat capable of being maintained at any temperature between 50°C. and 25°C., and the pressure of the toluene was observed at different temperatures within this range.

The toluene vapor was then pumped out of the bulb, air dried with phosphorus pentoxide was admitted, and the bulb was removed from the apparatus. A small amount of mercuric iodide⁶ having been introduced into it, the bulb was then sealed into an evacuating system, evacuated, sealed off and heated at 450°C. in an electric furnace for twelve hours. After this, the bulb was opened to the atmosphere and quickly put into place again to be evacuated. This time it was surrounded by an oil-bath heated to 150°C. and the mercuric iodide was thus removed from it by distillation. After the iodide had apparently all distilled away, the pumps were allowed to run for a period of about ten hours so as to remove completely all traces of the iodide vapor before dried air was again admitted to the apparatus. The bulb was then replaced in its original position in the thermostat, evacuated, toluene vapor introduced and another series of vapor pressure measurements carried out. All glass blowing was done thru phosphorus pentoxide and every precaution was taken for keeping water vapor away from the surface of the bulb.

The same procedure was carried out using another bulb and ammonium chloride⁷ instead of mercuric iodide.

¹ Loc. cit.

² Latham: *J. Am. Chem. Soc.*, **50**, 2987 (1928).

³ McHaffie and Lenher: loc. cit.

⁴ Frazer, Patrick and Smith: loc. cit.

⁵ Latham: loc. cit.

⁶ The mercuric iodide used here was prepared by precipitation, purified by sublimation, and dried in a desiccator over phosphorus pentoxide.

⁷ The ammonium chloride was prepared by subliming Baker's C. P. ammonium chloride three times. To dry it, the pure salt was placed in one end of a tube, the other end of which contained phosphorus pentoxide; the chloride was warmed several times daily for nine days. These special precautions were taken to dry the compound thoroughly in order to prevent its decomposition into ammonia and hydrogen chloride at a relatively low temperature.

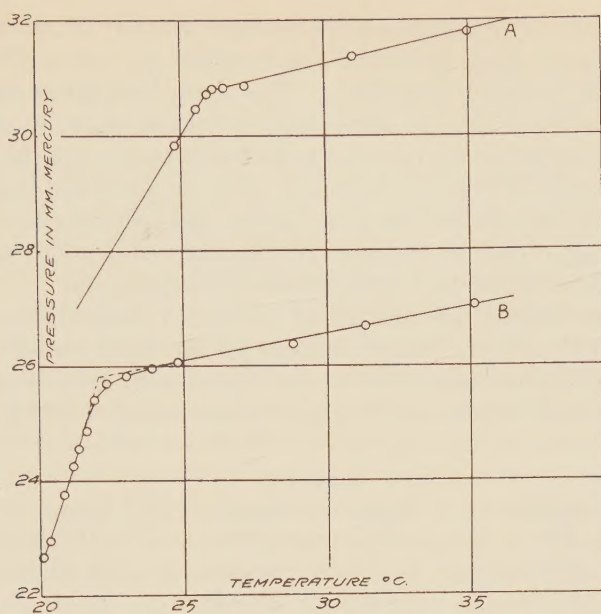


FIG. 1

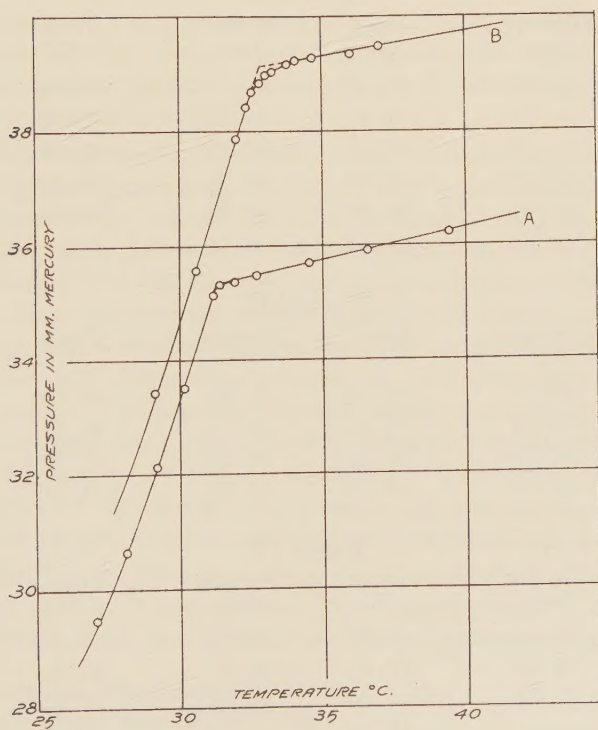


FIG. 2

The first series of measurements of the vapor pressure of toluene, obtained with a fused glass bulb, is given in Table I and the pressure is plotted against the temperature in Curve A of Fig. 1. The sharp break between the liquid and gas curves shows that no adsorption had taken place; in other words, in this case the surface of the bulb was molecularly plane. On the other hand, Table II and Curve B (Fig. 1) show that, after the glass had been heated in contact with mercuric iodide vapor, its surface had been attacked and roughened to such an extent as to cause considerable adsorption; the curve is markedly rounded off in the neighborhood of the dew-point.

Ammonium chloride was also found to have a decided effect on glass. Tables III and IV give the results obtained for the vapor pressure of toluene in a pyrex bulb before and after it was heated with ammonium chloride. The graphs of these results are shown in curves A and B of Fig. 2. In the

TABLE I

Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
40.04	37.82	32.22	36.82	30.93	36.73
36.00	37.41	31.50	36.83	30.56	36.41
33.58	37.04	31.10	36.83	29.74	35.84

TABLE II

Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
40.16	33.08	27.37	31.70	26.14	30.29
36.37	32.70	27.35	31.72	25.85	29.78
33.86	32.36	27.08	31.56	25.08	28.67
29.87	32.08	26.89	31.40	25.33	28.95
28.97	31.97	26.63	30.89	24.86	28.28
28.07	31.84	26.38	30.59		

TABLE III

Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
20.98	22.0	25.20	27.49	27.70	29.50
22.10	23.43	26.20	29.14	29.57	29.71
23.14	24.63	26.95	29.35	31.60	29.93
24.20	26.12	26.43	29.33	34.48	30.24

TABLE IV

Temp. °C	Pressure mm.	Temp. °C	Pressure mm.	Temp. °C	Pressure mm.
24.14	27.41	27.83	32.84	29.02	33.25
25.60	29.56	28.03	33.0	29.7	33.26
27.59	32.69	28.25	33.05	31.00	33.34
27.36	32.41	28.80	33.17	32.0	33.50
27.03	31.86				

case of ammonium chloride etching of the glass could be readily detected by the eye. In fact, in one bulb treated, where the temperature of the furnace was allowed to rise to 500°C . for a period of several hours, the effect was so great that it could be photographed.

In addition to the increased adsorptive power of glass produced by heating mercuric iodide in it, a further effect of this compound on glass must be noted. In the experiment with mercuric iodide, it was observed that a black residue remained in the bulb and black streaks were seen on the sides. This was not accidental. Several other pyrex tubes heated with mercuric iodide showed the same effect and some ground pyrex glass turned quite black when heated in contact with pure mercuric iodide. Some ground soft glass heated in the same way showed no change in color. The mercuric iodide was removed from the latter and the glass was boiled with water. The solution obtained in this way gave a positive test for iodide ion showing that the mercuric iodide had reacted with the soft glass. However, no test for iodide ion was given by a solution similarly obtained from ground pyrex glass, nor could the identity of the black substance be determined, altho its formation gave visible evidence that a reaction took place between the mercuric iodide and the pyrex.

Discussion

It has long been known that glass is by no means an inert substance but that it is attacked by many reagents, especially such highly polar ones as water and hydrogen chloride. A consideration of the chemical constitution of glass helps to explain this action.

Such studies on glass as have been made¹ show not only that it contains silicates as definite compounds but that it may be considered as a sponge of silica threads soaked in silicates and the products of their ionic dissociation. The silica apparently acts as a sort of solvent medium and it probably enters into combination with the silicates, producing solvation of the ions and salt molecules. Altho this reduces the ion mobilities to a great extent, Warburg² and Le Blanc and Kirschbaum³ have been able to measure the ionization of glass, and the latter found that soft glass is ionized to the extent of eighty percent at 250°C . The conduction is due to the transference of the sodium ion alone, the other constituents of glass being part of a rigid system. This conclusion was verified by Kraus and Darby.⁴ It is the presence of sodium ions dispersed thru the viscous mass of silica, silicates, and borosilicates, that enables one to account in some measure for the corrosive action mentioned.

The hydrolysis of glass is perhaps the most marked of these reactions especially at elevated temperatures. New vessels made of even the most resistant glasses, Jena and Pyrex, lose several milligrams in weight when

¹ W. E. S. Turner: "The Constitution of Glass" (1927).

² E. Warburg: *Ann. Physik*, **21**, 622 (1884).

³ Le Blanc and Kirschbaum: *Z. physik. Chem.*, **72**, 468 (1910).

⁴ Kraus and Darby: *J. Am. Chem. Soc.*, **44**, 278 (1922).

water is boiled in them for several hours¹ and those made of less resistant glasses are visibly etched and corroded. Sodium hydroxide is always found in the solution so made and it is quite likely that the reaction between the water and the glass is an ionic one since the temperature coefficient of water is very high and the proportion of sodium ions present in the glass also increases with the temperature. The electronegative hydroxyl ion from the water evidently reacts with the electropositive sodium ion in the glass. This conclusion is strengthened by the fact that the action of water is greatly diminished when the surface of the glass has been attacked sufficiently for it to become coated with a layer of silica.²

Hydrochloric acid also has a very special action on glass which has been studied by Foerster³ who found that the attack of concentrated solutions especially at high temperatures was very great. It may also be recalled in this connection that in one of the methods devised by Jannasch⁴ to decompose refractory silicates, the silicate is heated with hydrogen chloride under pressure between 200°C. and 250°C. Hydrogen chloride also contains a highly electronegative ion which tends to combine with sodium, and sodium chloride as well as silica were found in the residues obtained upon evaporation of a solution of 24.24% hydrochloric acid which had been boiled for several hours in a glass flask.⁵

Probably no glass has ever been made which is completely resistant to such chemical action. Pyrex glass has the most favorable composition for resistance to water and acid but even it is appreciably attacked by water and hydrochloric acid.⁶ Jena glass shows a behavior similar to that of pyrex.

Mercuric iodide may easily be placed in the category of highly polar compounds for, altho at ordinary temperatures it is but slightly ionized, it contains an electronegative halogen element. Rinse⁷ found that dissociation of the iodide took place at 450°C. and it seems a reasonable assumption that at this elevated temperature when the forces between the mercury and iodine were weakened, the iodine would enter into combination with the sodium ion in the glass. This assumption is justified by the experiment described in this paper in which a soluble iodide was found to have been formed when mercuric iodide was heated with soft glass. Even pyrex was attacked sufficiently for a marked change in its adsorptive power to be observed.

Furthermore, later results obtained by Rinse⁸ showed that he could obtain vapor pressure-temperature curves for mercuric iodide in which there were sharp breaks at the dew-point provided he did not first heat his apparatus to a high temperature. After he had once heated it above 500°C., he obtained

¹ Cauwood, English and Turner: *J. Soc. Glass Technology*, **1**, 153 (1917); Cauwood and Turner: **2**, 219 (1918).

² Mylius and Groschuff: *Z. physik. Chem.*, **55**, 101 (1907).

³ Foerster: *Z. anal. Chem.*, **33**, 299 (1894).

⁴ Jannasch: *Ber.*, **24**, 273 (1891).

⁵ Dimpleby, Cauwood and Turner: *J. Soc. Glass Technology*, **10**, 304 (1926).

⁶ International Critical Tables, **2**.

⁷ Smits and Rinse: *Rec. Trav. chim.*, **47**, 35 (1929).

Rinse: *J. Chem. Soc.*, **1928**, 1442.

continuous curves in every determination. It is very likely that the high temperature brought about some decomposition of the iodide and consequently a reaction between it and the glass took place.

The special action of mercuric iodide on pyrex producing the black compound is difficult to explain since the information obtained about it is very meager. Perhaps the fact that pyrex glass contains arsenic may be responsible for this action since Jena glass contains no arsenic and Rinse made no mention of having noticed similar behavior in experiments with the latter kind of glass.

That ammonium chloride should attack glass is also to be expected. Clarke and Steiger¹ demonstrated that dry ammonium chloride could be used to decompose the most refractory silicates, iron silicates resisting the action of strong hydrochloric acid being readily decomposed by the ammonium salt. In other cases, those of the zeolites, sodium was found to be quantitatively replaced by the ammonium radical. Ammonium chloride has also been proven a valuable reagent for testing the durability of glass. Its action may depend on its tendency to decompose into hydrogen chloride and ammonia; at the high temperature used in the experiment described here, even the dry salt tends to decompose to some extent.

Other continuous vapor pressure curves may be explained by similar action upon the glass surface. Measurements made by Rinse² indicated that iodine gave continuous curves while the curves for mercury showed sharp breaks at the dew-point. Here again it appears that the presence of an electronegative substance is necessary for attack upon glass.

It seems, then, rather improbable that any polar substance could be heated in glass without reacting to some extent with it. The surface of the glass after such action, no matter what pains had been taken beforehand to make it molecularly plane, would be so roughened that its extent could not be determined and calculation of the thickness of an adsorbed layer would be impossible. It may be said, therefore, that glass is not a suitable substance upon which quantitative studies of the extent of adsorption at high temperatures can be made unless the compound adsorbed can be proved to have no chemical action upon the glass.

Summary

1. Measurements of the vapor pressure of toluene in a fused pyrex bulb and in the same bulb after heating it with mercuric iodide show extensive adsorption in the latter case. This effect is attributed to the fact that mercuric iodide attacked the surface of the glass, leaving it coated with a layer of silica. The extent of the surface was then indeterminably great and no calculations of the thickness of the adsorbed layer could be made with accuracy.

¹ Clarke and Steiger: *Am. J. Sci.*, (4) **8**, 245 (1899); (4) **9**, 117 (1900); (4) **13**, 33 (1902)

² Rinse: *J. Chem. Soc.*, **1928**, 1442.

2. Mercuric iodide reacts with soft glass at a high temperature to produce a soluble iodide and with pyrex to form a black compound whose identity has not been determined.

3. Adsorption measurements also show that ammonium chloride has a great effect in roughening the surface of glass.

4. The corrosive action of mercuric iodide and of ammonium chloride has been compared with that of other chemical reagents, especially hydrogen chloride. This action has been attributed to the existence of free sodium ions in the glass and has been shown to render glass an unsuitable substance for use in adsorption vessels where the adsorption of polar compounds at high temperatures is to be studied.

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BIOGRAPHY

Clara Emilie Miller was born in Baltimore, Maryland, on February 29, 1904, and received her elementary and secondary education in the public schools of that city. In 1923, she was graduated from the Goucher College with a Bachelor of Arts degree and she received her Master of Arts degree from The Johns Hopkins University in 1925. The years 1925-1927 and the first term of 1928-1929, were spent as an instructor in chemistry at the Margaret Morrison Carnegie College of the Carnegie Institute of Technology. She was granted leaves of absence from that school for the session 1927-1928 and the second term of 1928-1929, and during that time was enrolled again at the Johns Hopkins University where she carried out her research work. Part of this work was also done at the Margaret Morrison Carnegie College. Her course was completed in June 1930.

She held a Goucher College Fellowship in the Johns Hopkins University for the session 1923-1924 and a Hopkins Scholarship for 1927-1928

